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PII: S0045-6535(18)30432-6

DOI: 10.1016/j.chemosphere.2018.03.027

Reference: CHEM 20971

To appear in: *ECSN*

Received Date: 15 December 2017

Revised Date: 27 February 2018

Accepted Date: 4 March 2018

Please cite this article as: Urtiaga, A., Soriano, A., Carrillo-Abad, J., BDD anodic treatment of 6:2 fluorotelomer sulfonate (6:2 FTSA). Evaluation of operating variables and by-product formation, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.03.027.

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BDD Anodic Treatment of 6:2 Fluorotelomer Sulfonate (6:2 FTSA). Evaluation of Operating Variables and By-Product Formation

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Revised manuscript submitted to Chemosphere

Special Issue EAOPs-POPs

February 2018

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ABSTRACT

The concerns about the undesired impacts on human health and the environment of long chain perfluorinated alkyl substances (PFASs) have driven industrial initiatives to replace PFASs by shorter chain fluorinated homologues. 6:2 fluorotelomer sulfonic acid (6:2 FTSA) is applied as alternative to PFOS in metal plating and fluoropolymer manufacture. This study reports the electrochemical treatment of aqueous 6:2 FTSA solutions on microcrystalline BDD anodes. Bench scale batch experiments were performed, focused on assessing the effect of the electrolyte and the applied current density (5-600 A m^{-2}) on the removal of 6:2 FTSA, the reduction of total organic carbon (TOC) and the fluoride release. Results showed that at the low range of applied current density (J=50 A m^{-2}), using NaCl, Na_2SO_4 and $NaClO_4$, the electrolyte exerted a minimal effect on removal rates. The formation of toxic inorganic chlorine species such as ClO_4^- was not observed. When using Na_2SO_4 electrolyte, increasing the applied current density to 350-600 A m^{-2} promoted a notable enhancement of the 6:2 FTSA removal and defluorination rates, pointing to the positive contribution of electrogenerated secondary oxidants to the overall removal rate. 6:2 FTSA was transformed into shorter-chain PFCAs, and eventually into CO_2 and fluoride, as TOC reduction was > 90%. Finally, it was demonstrated that diffusion in the liquid phase was controlling the overall kinetic rate, although with moderate improvements due to secondary oxidants at very high current densities.

Keywords: 6:2 FTSA, BDD, electrolysis, Perfluorinated alkyl substances, PFHxA, fluorochemicals

1. INTRODUCTION

There is an international recognition of long chain perfluorocarboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, n≥7) and perfluoroalkane sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$, n≥7) as global contaminants, as a result of their high persistence and bioaccumulative properties (Stockholm Convention, 2009; ECHA, 2013). The concerns about the undesired impacts on human health and the environment has driven industrial initiatives to phase out long chain perfluoroalkyl substances (US EPA, 2006) that are being substituted by products based on shorter perfluoroalky chains such as perfluorobutane sulfonate (PFBS) and fluorotelomer-based substances (Wang et al., 2013). 6:2 fluorotelomer sulfonic acid (6:2 FTSA, $C_6F_{13}CH_2CH_2SO_3H$) is applied as alternative to PFOS in the surface treatment of metal and plastic components, and as processing aid in emulsion polimerization of fluoropolymers (Brunn-Poulsen et al., 2011). 6:2 FTSA is also known to be the major degradation product from fluorotelomer sulfone and mercaptan chemistry used in telomer-based air fire fighting foams (AFFF) (Cheremisinoff, 2017). The C-C bonds of carbons substituted by hydrogen and the C-S bond make 6:2 FTSA much more susceptible to biodegradation compared to refractory PFCAs and PFSAs. Regarding the aquatic toxicity, a recent study concluded that 6:2 FTSA is not bioaccumulative, and that it poses minimal risk to aquatic organisms (Hoke et al., 2015). Even though, 6:2 FTSA may still pose risks as its aerobic biotransformation in wastewater treatment plants is slow and the main stable biodegradation product is perfluorohexanoic acid (PFHxA), a short chain PFCA that behaves as persistent in the environment as the long chain homologues (Wang et al., 2011). An annual average environmental quality standard (AA-EQS) of 1 mg L^{-1} for PFHxA in freshwaters has been recently proposed (Valsecchi et al., 2017).

Because of the persistence of its degradation products, 6:2 FTSA cannot be mineralized by conventional biological water treatments. Therefore, new advanced oxidation processes (AOPs) are being studied for the removal of this polyfluorinated substance from polluted waters. Fernandez et al. (2016) reported that less than 20% of fluoride was released in the sonolysis treatment of 6:2 FTSA (initial concentration 130 μM). The use of ozone and hydrogen peroxide oxidation was investigated by Yang et al. (2014) who selected UV/H_2O_2 as the most effective technology among various AOPs investigated. Heat activated persulfate achieved fast 6:2 FTSA oxidation, with PFHxA being the dominant stable product (Park et al., 2016). Recent progress on electrochemical oxidation (ELOX) reveled the high efficiency of boron doped diamond (BDD) anodic electrolysis for the treatment of industrial wastewaters generated in the chemical manufacture of side-chain-fluorinated polymers and fluorotelomer based products for fire-fighting foams (Urtiaga et al., 2015; Gomez-Ruiz et al., 2017a). 6:2 FTSA and 8:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) were completely removed from the effluent of the wastewater treatment plant, and the group of PFCAs, PFHxA being the most abundant, were also progressively mineralized to achieve 99.74% of total poly and perfluoroalkyl substances (PFASs) removal. Similarly, Soriano et al. (2017) reported the significant reduction of energy consumption by means of membrane pretreatment followed by BDD electrochemical oxidation in the treatment of process waters containing high concentrations of PFHxA. To date, the electrochemical treatment of 6:2 FTSA on dimensionally stable anodes (DSA) has been reported to achieve low decomposition ratios of approximately 30%, and to yield increasing concentrations of PFHxA as final oxidation product (Zhuo et al., 2014). Therefore, DSA electrooxidation did not achieve mineralization and defluorination of 6:2 FTSA.

The overall goal of this study was to evaluate and demonstrate the efficient electrochemical degradation of 6:2 FTSA with BDD electrodes. Aqueous solutions prepared from 6:2 FTSA formulations that are commercialized as surfactants for surface treatment operations and emulsion polymerization were investigated. Experiments examined the effects of the type of electrolyte, using sulfate, chloride and perchlorate salts, on 6:2 FTSA defluorination and mineralization, by means of the total organic carbon (TOC) removal. The influence of the main operation parameter, e.g.: the applied current density, from 5 - 600 A m^{-2}, on reaction rates and on the generation and degradation of shorter chain perfluorinated intermediate products was studied. Treatment of individual PFCAs was also assessed, in order to validate the proposal of kinetic regime.

2. MATERIALS AND METHODS

6:2 FTSA solutions were prepared from CAPSTONE FS-10© (Chemours), a commercial concentrated 6:2 FTSA aqueous solution. Perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$), perfluorohexanoic acid (PFHxA, $C_5F_{11}COOH$) and perfluoropentanoic acid (PFPeA, C_4F_9COOH) were purchased from Sigma Aldrich Chemicals. All perfluorocarboxylic acids were reagent grade or higher and were used as received without further purification. NaCl (Panreac), Na_2SO_4 (Panreac) and $NaClO_4$ (Sigma-Aldrich) were used to prepare the electrolyte solutions. All solutions were prepared using ultrapure water (Q-POD Millipore). Methanol (UHPLC-MS grade) was obtained from Scharlau.

The electrooxidation experimental set-up consisted of an electrochemical cell (DiaCell 201 PP, Adamant Technologies), a power supply (Vitecom 75-HY3005D), a jacketed feed tank, and a cooling bath (Polyscience 9510). The cell contained two parallel flow-

by compartments made of a central bipolar p-Si/BDD electrode and p-Si/BDD anode and cathode, with an interelectrode gap of 1 mm in each channel. Each electrode had a surface area of 70 cm^2, resulting in a total anodic area of 140 cm^2. 2 L aqueous solutions of 6:2 FTSA (100 mgL^{-1}), or individual perfluorocarboxylic acids, were used as feed in the experiments that were conducted in batch mode at constant temperature of 20 ºC. The experiments were carried out in batch mode and galvanostatic conditions. Further details on the experimental system can be found elsewhere (Urtiaga et al., 2014; Soriano et al., 2017). The applied current density (J) was varied in the range 5 - 600 A m^{-2}. Treated samples were collected in polypropylene containers, and preserved at 4 ºC until analysis.

Total organic carbon (TOC) analyses were performed using a TOC-V CPH (Shimadzu). Fluoride was analyzed by ion chromatography (Dionex 120 IC) provided with an IonPac As-HC column and using a 9 mM Na_2CO_3 solution as eluent, that was circulated at a flowrate of 1 $mLmin^{-1}$, based on Standard Methods 4110B (APHA, 1998). The limit of quantification (LOQ) for fluoride analysis was 0.03 mgL^{-1}.

The analyses of 6:2 FTSA and its degradation products PFHpA, PFHxA, PFPeA and PFBA were carried out by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS). Prior to instrumental analysis samples were extracted by a solid-phase extraction (SPE) procedure in order to eliminate dissolved salts. Non-filtered samples were diluted prior to SPE in 2% formic acid in order to acidify samples. TELOS neo WAX SPE cartridges (200 mg, 6 mL; Kinesis, U.K.) were conditioned with methanol and subsequently equilibrated with ultrapure water (Milli-Q, Millipore) before sample loading. Two interference elution wash steps were carried out separately with 3 mL Milli-Q water each one to eliminate ionic interferences. Finally, target analytes were eluted with 2 mL of methanol: ammonium

hydroxide (95:5 v/v). The extracts were further evaporated until dryness under a gentle stream of dry nitrogen gas. The final volume was adjusted to 1 mL Milli-Q water and filtered (0.22 μm) prior to injection. Recovery rates of the SPE procedure were determined by applying the detailed method to spiked Milli-Q water samples (n=6) with target analyte standard solutions (6:2 FTSA, 100 mg L^{-1}; PFHpA, PFHxA, and PFPeA, 10 mg L^{-1}, each one) and Na_2SO_4, 5 g L^{-1}. Percent recovery rates were as followed: 6:2 FTSA, 91.4 ± 8.8; PFHpA, 93.4 ± 14.4; PFHxA, 118.1 ± 10.6; PFPeA, 92.5 ± 19.6.

The purified sample extracts were analyzed using an UPLC-TQD system (Waters, Milford, MA, USA) with an electrospray ionization (ESI) interface operated in the negative ionization mode. An Acquity UPLC BEH C18 column (50 x 2.1 mm x 1.7 μm) at 50 ºC was used for the analytical separation. The mobile phase consisted of 5% methanol containing 2 $mmolL^{-1}$ ammonium acetate (A) and methanol (B), at an operating flow rate of 0.4 $mLmin^{-1}$ in gradient mode.

Dilutions from the stock standard solutions were prepared in water at 7 concentration levels ranging from 1 ng mL^{-1} to 400 ng mL^{-1} and calibration curves were built in order to calculate the PFASs concentrations in real samples and to control the linear range of the instrumental response. Quality control and validation of the method were made using recovery rates, method blanks, calibration linearity, mass detection limits and quantification limits. LOQs were 1 ng mL^{-1} in real samples.

3. RESULTS AND DISCUSSION

Initial experiments were aimed at the analysis of the effect of the electrolyte on the 6:2 FTSA mineralization. Three electrolyte solution were tested: Na_2SO_4 (5 gL^{-1}), NaCl (3.5 gL^{-1}), and $NaClO_4$ (9.4 gL^{-1}), working at J=50 Am^{-2}. The concentration of each salt was selected to provide the electrolyte solution with a similar background conductivity

(6.9 $mScm^{-1}$). While perchlorate salts are known to behave as inert electrolytes in BDD electrooxidation (Chaplin et al., 2011), sulfate and chloride have been reported to act as promoters of secondary oxidizing species such as active chlorine, sulfate radical or persulfate anion (Martín de Vidales et al., 2015; Uranga-Flores et al., 2015; Jalife-Jacobo et al., 2016; Lan et al., 2017). Nevertheless, Figure 1a shows no significant influence of the type of electrolyte on TOC kinetics removal, for a 100 mgL^{-1} 6:2 FTSA solution, revealing that the formation of secondary oxidants with potential ability to degrade 6:2 FTSA and its secondary degradation products did not occur at the low range of applied current density (J=50 A m^{-2}) used in this group of experiments. Similarly, the release of fluoride anions observed in Figure 1b, that resulted from the cleavage of C-F bonds in the perfluorocarboxylic chain of 6:2 FTSA, supports the effective mineralization of the fluorotelomer sulfonate compound into CO_2 and fluoride. A slightly slower fluoride release is observed for NaCl electrolyte solution, in good correspondence with the TOC evolution. This behavior can be attributed to the partial use of the applied current for the anodic oxidation of chloride to chlorine (Cabeza et al., 2007; Urtiaga et al., 2012).

Using the NaCl electrolyte turned into free chlorine and chlorate generation, as it is depicted in Figure 2, although it is worth mentioning that perchlorate formation was not observed. Free chlorine did not have enough oxidative power to decompose perfluorinated compounds as shown in Figure 1. These results contrast with previously reported BDD degradation of diazo dyes (Jalife-Jacobo et al., 2016) and naphtenic acids (Diban and Urtiaga, 2018), where active chlorine species formed upon chloride oxidation significantly enhanced the kinetics of the organic compounds removal. Nevertheless, in accordance to the results of the present study, Schaefer et al. (2017) proved that chloride had a minimal effect on BDD electrochemical removal of

perfluorooctanoic acid and perfluorooctane sulfonic acid, showing that the electrogenerated active chlorine does not degrade perfluorinated compounds. Perchlorate formation by BDD anodic oxidation has been largely reported for sodium chloride electrolytes (Bergmann et al., 2009; Azizi et al., 2011; Urtiaga et al., 2014), although perchlorate generation is also known to be delayed at high chloride concentrations (Perez et al., 2012) and low applied current densities (Pipi et al., 2016; Gomez-Ruiz et al., 2017a). The low current density (J=50 Am^{-2}) applied in the experiments of Figure 1 explains the low chlorate development and the absence of perchlorate generation.

Sulfate release could be also observed in experiments performed using NaCl and $NaClO_4$ electrolytes. The C-S bond between the unfluorinated carbon of the alkyl chain and the sulfonic end group ($-CH_2-SO_3^-$) makes 6:2 FTSA easily susceptible to oxidation. Results pointed to the total release of the sulfate group contained in the 6:2 FTSA molecule, although the quantitation was adversely affected by the large sample dilution that was needed in order to avoid the saturation of the conductivity detector in the ion chromatography system. For example, using NaCl as electrolyte, the electrochemical treatment of 6:2 FTSA (100 mg L^{-1}, J=50 A m^{-2}) gave rise to 24 mg L^{-1} of sulfate in the treated water, that is equivalent to the total amount of oxidized sulfur contained in the initial feed.

The effect of the applied current density on 6:2 FTSA treatment is shown in Figures 3 and 4. Both TOC removal and fluoride release became progressively faster when increasing the applied current in the range 5 – 600 A m^{-2}. TOC removals at the low J range, 5 – 20 A m^{-2}, followed zeroth-order trends, although a remarkable enhancement of the TOC removal rate was observed when increasing the applied current in that range. Both features point to a current control regime of the removal kinetics in the low

J range. In contrast, increasing the applied current to 50 – 600 A m^{-2} modified the apparent TOC removal kinetics to first-order, which is associated to a diffusion control kinetic regime. Moreover, increasing the applied current from 50 to 600 A m^{-2} granted moderate improvements in the kinetic rates of TOC disappearance. It is worth mentioning that the effect of varying the applied current density had a stronger influence on the kinetics of fluoride release (Figure 3c). This behavior could be indicating a beneficial effect of the applied current on the removal of the secondary products, perfluorocarboxylic acids, that were obtained upon degradation of 6:2 FTSA, as it will be discussed later on. In terms of energy consumption, the plot (Figure 3b) of TOC removal vs. the specific charge passed (*Q*, A h L^{-1}) indicates that the optimal range of applied current for the BDD electrochemical treatment of 100 mgL^{-1} 6:2 FTSA solutions is between 20 and 100 A m^{-2}; the upper value would imply a moderately higher energy consumption, but with the advantage of reducing the treatment time.

Figure 4 shows the progress of 6:2 FTSA during BDD electrooxidation at *J* values from 20 to 600 A m^{-2}. Three distinct zones can be distinguished. Increasing the applied current from 20 to 50 A m^{-2} produced an increase in the kinetics of 6:2 FTSA degradation, although further increase of *J* to 100 A m^{-2} did not provide any further improvement. Distinctively, increasing the applied current to 350 and 600 A m^{-2} had a remarkable positive effect on the kinetics of 6:2 FTSA removal, a behavior that can be assigned to the oxidative action of electrogenerated secondary oxidants as a result of sulfate oxidation and reduction reactions to form sulfate radicals ($SO_4^{\cdot-}$) and peroxidisulfate ($S_2O_8^{4-}$), respectively (Davis et al., 2014; Sopaj et al., 2015).

Perfluorocarboxylic acids that were obtained as degradation products of 6:2 FTSA are plotted in Figure 5 (for conciseness, only data obtained at 20, 100 and 600 A m^{-2} are displayed). At any *J*, PFHxA was the product observed at a highest concentration

(PFHxA values should be read in the right hand side Y-axis). The maximum PFHxA concentration was observed at earlier treatment times as the applied current was increased. Other PFCAs (PFHpA, PFPeA and PFBA) were observed at lower concentrations than PFHxA, typically below 1 mgL^{-1}, and their content was clearly reduced as the applied current density was increased. PFCAs smaller than PFBA are volatile compounds and cannot be determined in the liquid samples. Remarkably, the formation of PFHpA is observed at much lower concentration than PFHxA, in good agreement with the observations reported by Park et al. (2014) for heat activated persulfate oxidation of 6:2 FTSA. These results can be explained by the preferential attack of hydroxyl radicals to the $-CH_2-$ group attached to the perfluoroalkyl chain. Shorter chain PFPeA and PFBA are formed upon the loss of successive CF_2 units in consecutive steps (Gomez-Ruiz et al., 2017b; Schaefer et al., 2017). The results of analyzed PFASs also explains the faster kinetics of 6:2 FTSA disappearance compared to the TOC removal rate, related to the extra energy needed for the degradation of PFCAs obtained as secondary products.

The kinetics of the removal of perfluorocarboxylic acids PFHpA, PFHxA, PFPeA were further explored. In a trial to facilitate the observation of the oxidation by products, and also to avoid the conditions needed for the formation secondary oxidants, the applied current was intentionally maintained at a low value, J = 20 Am^{-2}. Experiments were performed starting with solutions of one single PFCA: PFHpA, PFHxA or PFPeA, with an initial concentration of 100 mgL^{-1} in every case. 6:2 FTSA removal is included for comparison. Concentration data in Figure 6 show that the kinetic removal was only slightly faster as the molecular size was decreasing. These results can be explained by the diffusion control kinetic regime, that is moderately faster as the molecular size of the PFASs compound is reduced. It means that the degradation reaction occurring at the

electrode is faster than the diffusion of the compounds moving from the liquid bulk towards the electrode vicinity. The high fast reactivity of the hydroxyl radical mediated oxidizing reactions and direct electron transfer at the anode surface prevents the intermediate compounds of diffusing from the proximity of the anode towards the liquid bulk, and therefore, the observed concentrations of degradation products are always much lower than those predicted from the apparent kinetic constants obtained in individual experiments.

4. CONCLUSIONS

The electrochemical treatment of 6:2 FTSA by means of microcrystalline boron doped diamond electrodes has been studied. Results herein presented demonstrated that 6:2 FTSA is electrochemically degraded, with removal rates that approach 100%. 6:2 FTSA was transformed into perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA), although PFHxA appeared at a much higher proportion than PFHpA. Effective mineralization was obtained, as demonstrated by the high TOC and defluorination rates achieved (>90%). The overall kinetics of 6:2 FTSA removal was controlled by the diffusion in the liquid phase in the low range of applied current density. However, increasing the applied current density resulted in faster removal rates, that were assigned to the role of strong electrogenerated oxidants from sulfate electrolyte. At any current density conditions, minority detection of perfluorocarboxylic acids in the liquid bulk was observed, showing that the secondary products were retained in the proximity of the anode surface to be rapidly degraded. Overall, this results poses BDD electrochemical treatment as effective technology for the treatment of 6:2 FTSA, used nowadays as substitute on perfluorooctane sulfonate (PFOS) in metal plating and fluorotelomer manufacture.

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ACKNOWLEDGEMENTS

Support from MINECO and SPAIN-FEDER 2014–2020 to project CTM2016-75509-R and to the Spanish Excellence Network E3TECH (CTQ2015-71650-RDT) is acknowledged. J. Carrillo-Abad thanks the Generalitat Valenciana for granting a post-doctoral fellowship (APOSTD/2015/019). The authors are thankful to Dr. R. Buck (Chemours Co.) for kindly providing samples of Capstone FS10.

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Figure captions

Figure 1. (1.5-column fitting image) Effect of electrolyte on 6:2 FTSA mineralization and defluorination. Fractional TOC (a) and fluoride release (b). Initial concentrations $[6:2\ FTSA]_0$ = 100 mg L^{-1}, $[TOC]_0$ = 22.5 mg L^{-1}. *J*= 50 A m^{-2}.

Figure 2. (single column fitting image) Distribution (mol%) of inorganic chlorine species during the BDD electrochemical treatment of 6:2 FTSA, when using NaCl as electrolyte. [NaCl] = 3.5 gL^{-1}. $[6:2\ FTSA]_0$ = 100 mgL^{-1} , *J*=50 A m^{-2}. Total chlorine was maintained constant along the experimental time.

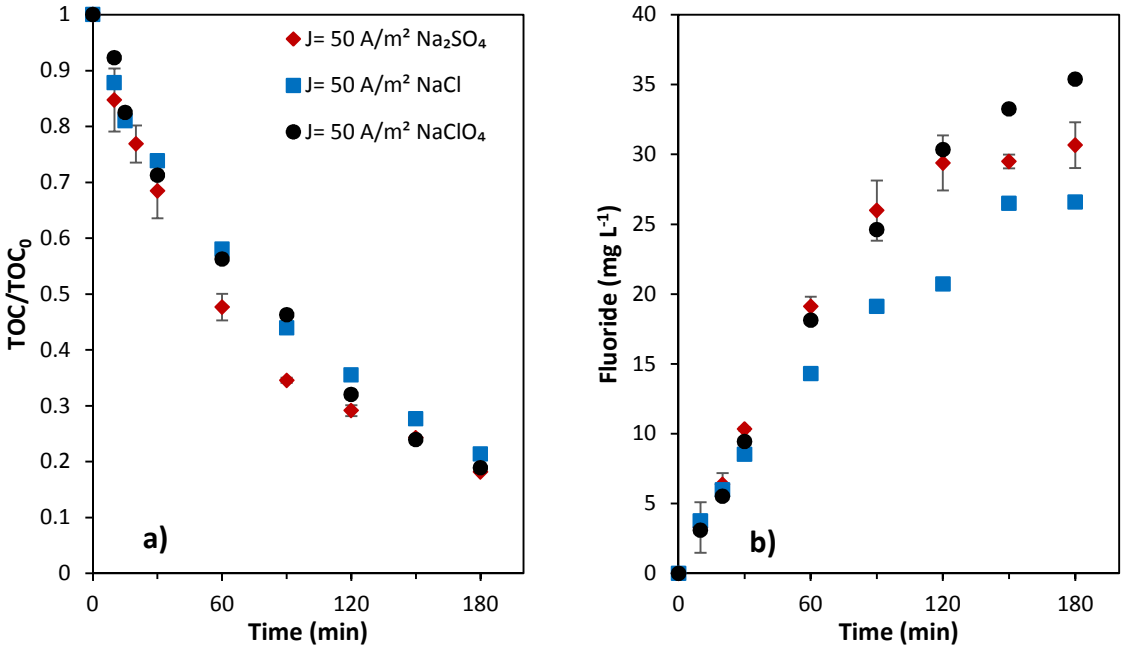
Figure 3. (1.5-column fitting image) Effect of the applied current on the removal of fractional TOC with time (a), Fluoride release (b), and TOC reduction as a function of the specific charge passed *Q* (c). $[6:2\ FTSA]_0$ = 100 mg L^{-1}, $[TOC]_0$ = 22.5 mg L^{-1}.

Figure 4. (single column fitting image) Effect of applied current density on fractional 6:2 FTSA removal. $[6:2\ FTSA]_0$=100 mgL^{-1}. Dotted lines are 1^{st}-order exponential fittings of experimental data.

Figure 5. (1.5 column image) Short chain perflurocarboxylic acids (PFHpA, PFHxA, PHPeA and PFBA) obtained as secondary products of 6:2 FTSA BDD electrooxidation. (a) *J*=20 A m^{-2}; (b) *J*= 100 A m^{-2}; (c) *J*=600 A m^{-2}. $[6:2\ FTSA]_0$ = 100 mg L^{-1}.

Figure 6. (single column image) Removal of different PFASs. Initial concentration 100 mgL^{-1} for every perfluoroalkyl substance. *J*=20 A m^{-2}.

FIGURE 1



BLACK AND WHITE VERSION

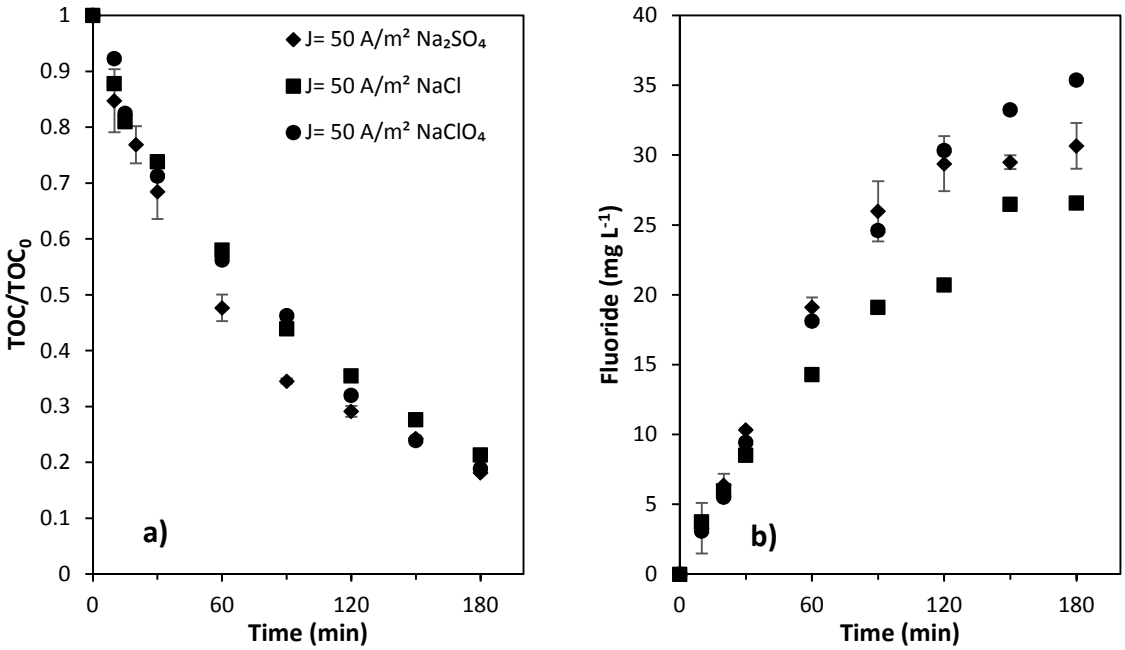
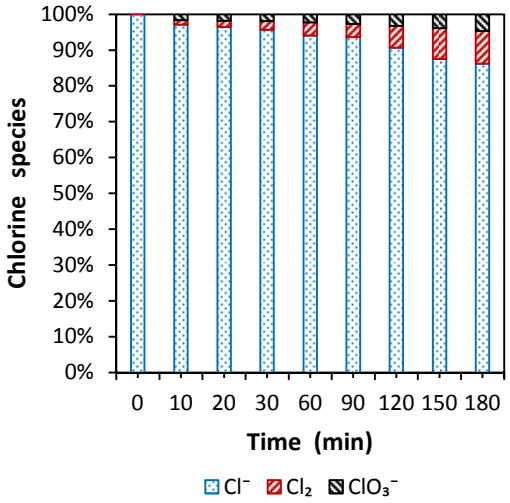


FIGURE 2



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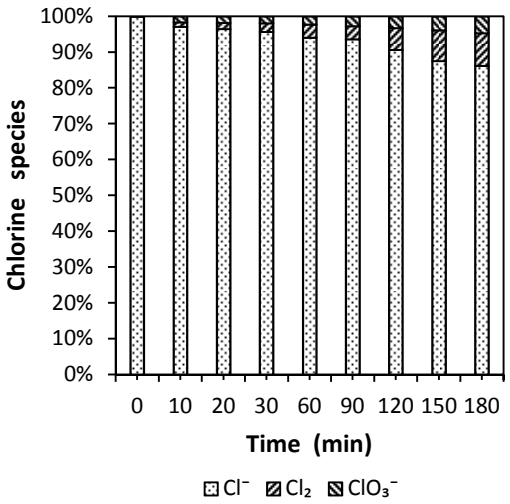


FIGURE 3

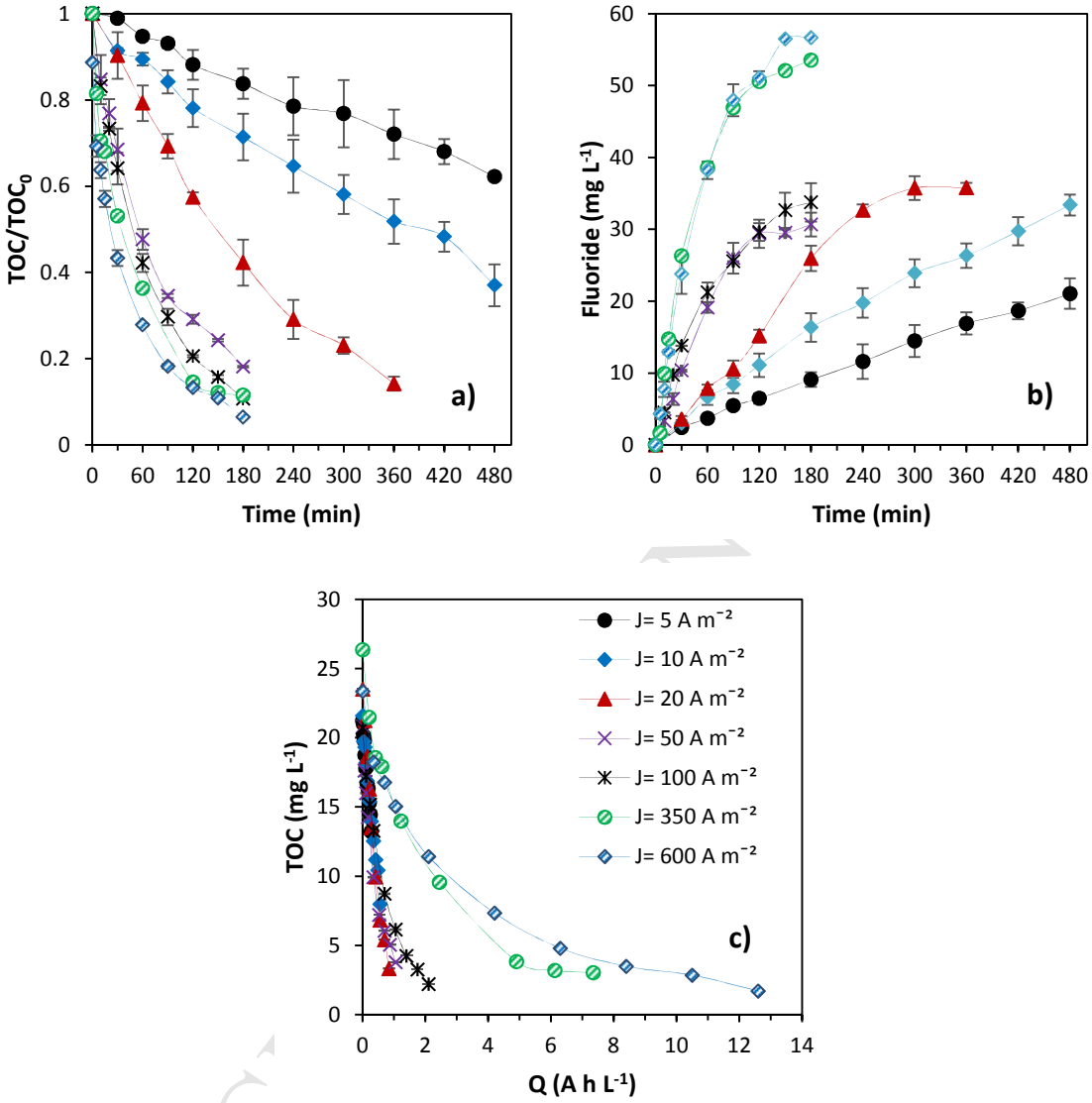

TOC/TOC0
Time (min)
a)
Fluoride (mg L-1)
Time (min)
b)
TOC (mg L-1)
Q (A h L-1)
c)
J= 5 A m-2
J= 10 A m-2
J= 20 A m-2
J= 50 A m-2
J= 100 A m-2
J= 350 A m-2
J= 600 A m-2

FIGURE 3

BLACK AND WHITE VERSION

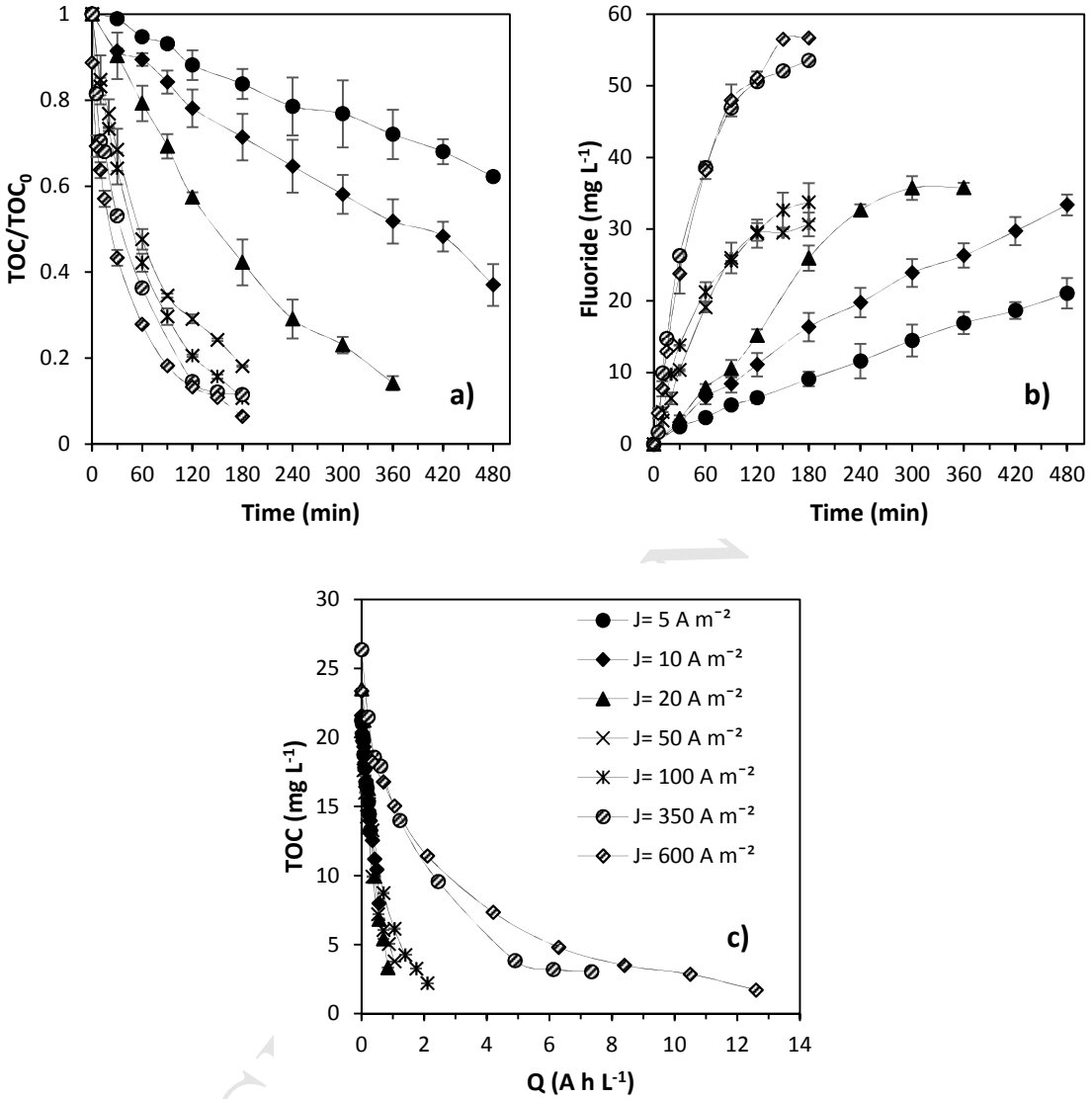
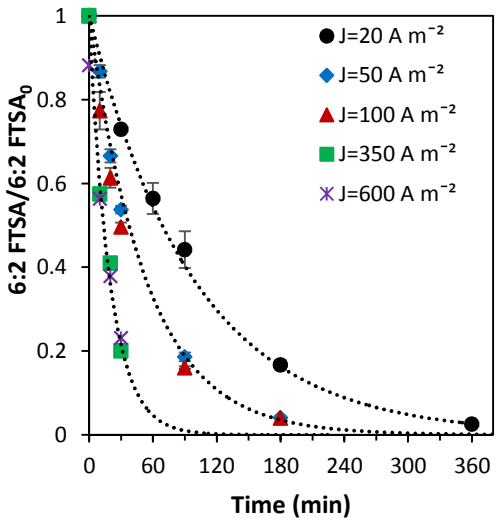


FIGURE 4



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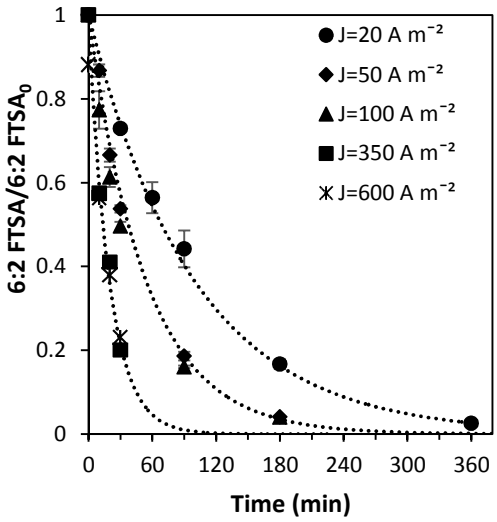


FIGURE 5

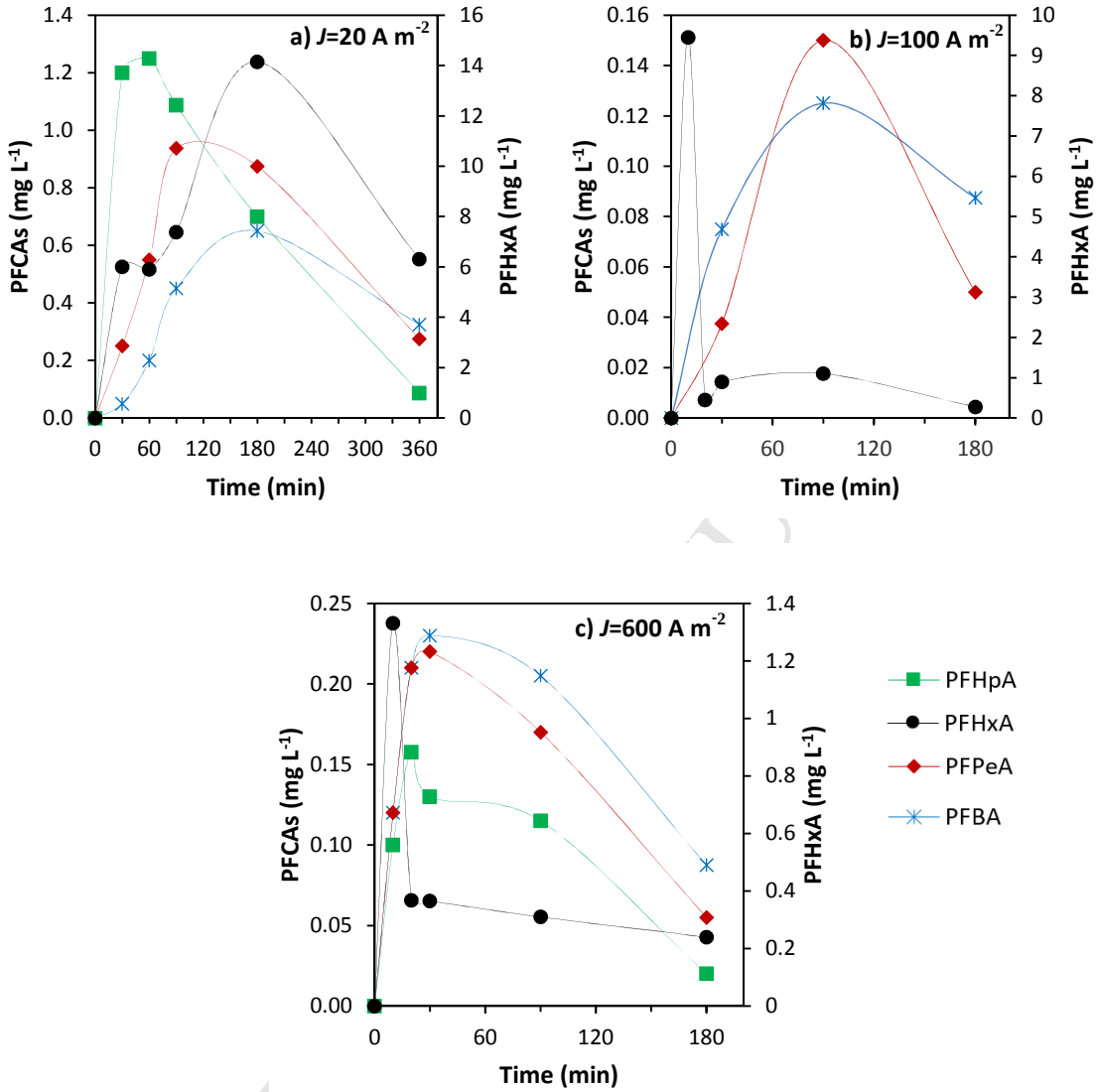

a) J=20 A m-2
b) J=100 A m-2
c) J=600 A m-2
PFCAs (mg L-1)
PFHxA (mg L-1)
Time (min)
PFHpA
PFHxA
PFPeA
PFBA

FIGURE 5

BLACK AND WHITE VERSION

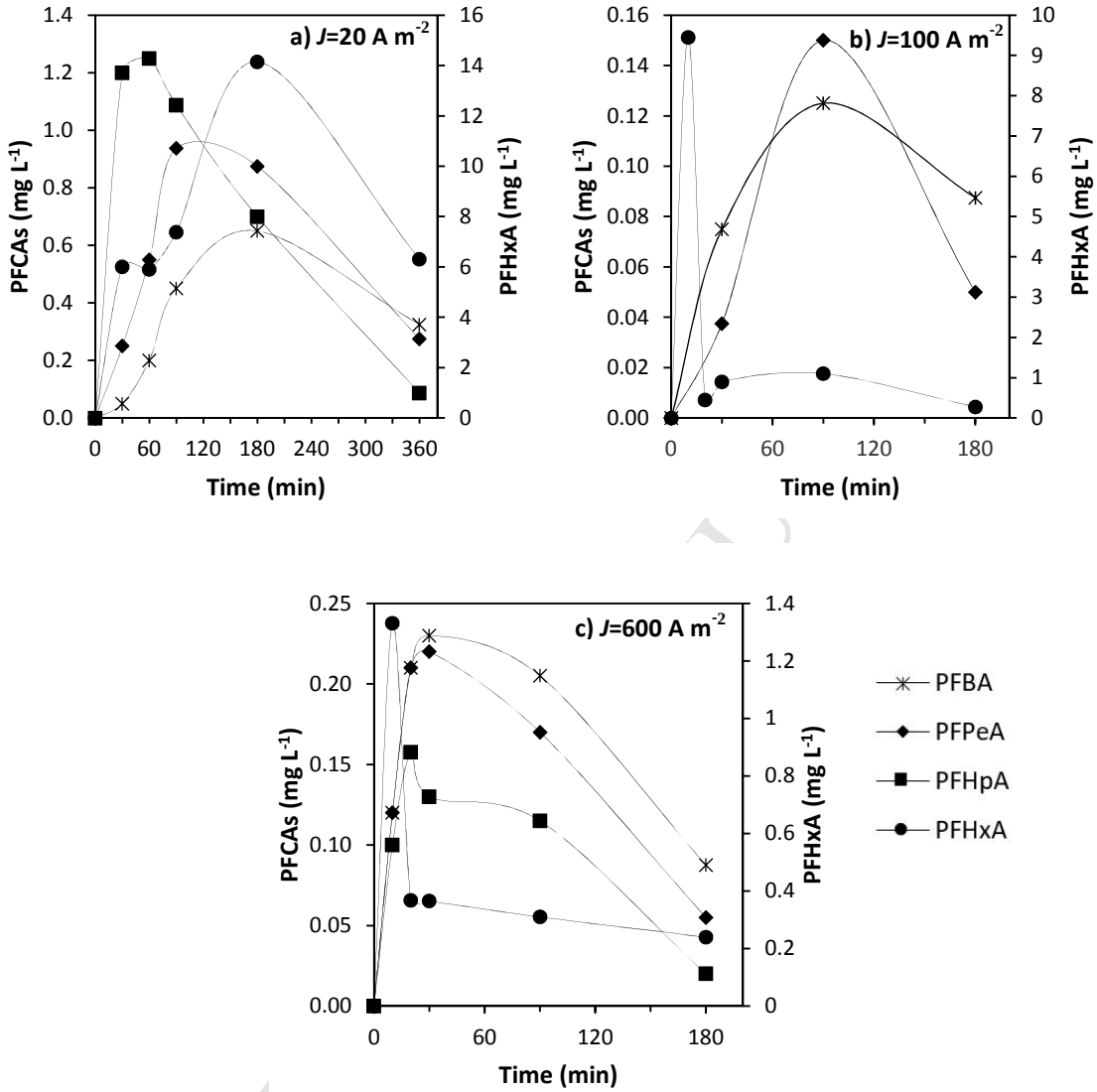
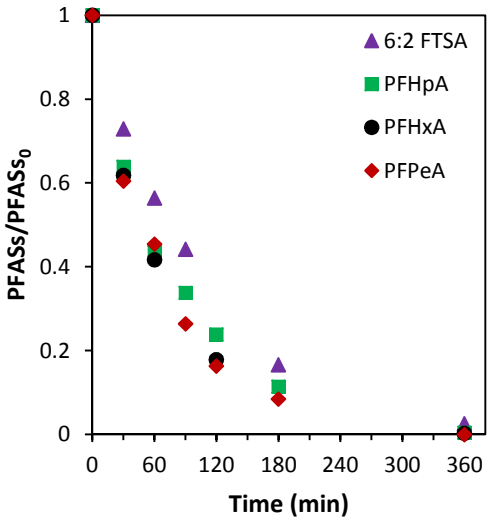


FIGURE 6



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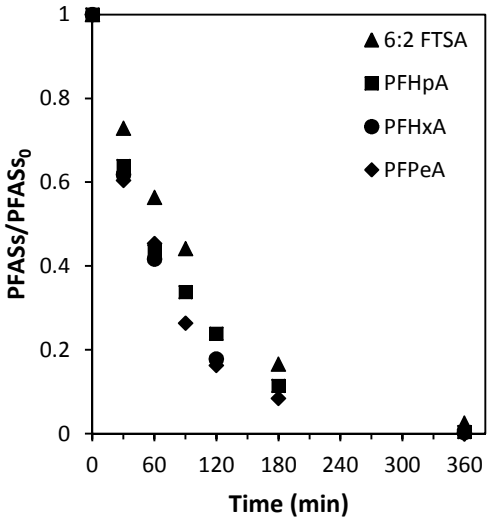

- 6:2 FTSA is completely removed by electrolysis with BDD anodes
- 6:2 FTSA degradation results in the formation of PFHxA and shorter chain PFCAs
- PFHxA is completely defluorinated and decarboxylated
- Mineralization higher than 90% is attained after passing 2 kAh m^{-3}

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